

Performance evaluation of newly developed portable aerosol sizers used for nanomaterial aerosol measurements

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Abstract: Nanomaterial particles exhibit a wide range of sizes through the formation of agglomerates/aggregates. To assess nanomaterial exposure in the workplace, accurate measurements of particle concentration and size distribution are needed. In this study, we evaluated the performance of two recently commercialized instruments: a portable scanning mobility particle sizer (SMPS) (NanoScan, TSI Inc.), which measures particle size distribution between 10 and 420 nm and an optical particle sizer (OPS, TSI Inc.), which measures particle size distribution between 300 and 10,000 nm. We compared the data measured by these instruments to conventional instruments (i.e., a widely used laboratory SMPS and an optical particle counter (OPC)) using nano-TiO₂ powder as test aerosol particles. The results showed obvious differences in the size distributions between the new and old SMPSs. A possible reason for the differences is that the cyclone inlet of the new SMPS (NanoScan) acted as a disperser of the weakly agglomerated particles and consequently the concentration increased through the breakup of the agglomerates. On the other hand, the particle concentration and size distributions measured by the OPS were similar to the OPC. When indoor aerosol particles were measured, the size distribution measured by the NanoScan was similar to the laboratory SMPS.

Key words: Nanomaterials, Agglomerates, Portable aerosol sizer, Scanning mobility particle sizer, Optical particle counter, Titanium dioxide

Introduction

Nanomaterials, designed on the nano-scale (1–100 nm), have specific functional physical and chemical properties. They are used for various products, adding or improving a function¹⁾. However, there is growing concern regarding their possible adverse health effects²⁾ through exposure during handling in the workplace.

The concentrations of nanomaterial aerosol particles and their size distributions are essential when considering the particle dynamics in the workplace air, the exposure control plan, and the risk assessment. Different real time aerosol sizers measuring particle concentration and size distribution are currently commercially available. They have great advantages, since they are easy to use and the data can be checked on site. Therefore, their use is recommended for an initial screening of nanomaterial exposure^{3,4)}.

However, there are some difficulties in measuring the size distribution of nanomaterial aerosol particles, because nano-sized particles generally form agglomerates caused

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Table 1. Specification of aerosol measuring instruments

	Optical particle counters		Scanning mobility particle sizers	
	OPS (newly developed)	OPC	NanoScan (newly developed)	SMPS
Model	Model 3330, TSI Inc.	KR-12A, Rion Co.	Model 3910, TSI Inc.	Model 3936L10, TSI Inc.
Measuring range (nm)	300–10,000	300–>5,000	10–420	10–1,000 (variable)
Size channels	16	6	13	64 per decade
Number concentrations (cm ⁻³)	<3,000	<70	10 ² –10 ⁶	1–10 ⁷
Sample flow rate (L min ⁻¹)	1.0	2.83	0.75	1.0
Weight of instrument (kg)	2.6	1	9	36
Battery life (h)	12	8	12	– (AC drive)

by interparticle forces, such as liquid bridges, van der Waals, and electrostatic forces, so that the agglomerates exhibit a wide range of sizes (nanometer to micrometer). Therefore, to monitor the concentrations and size distributions of nanomaterial aerosol particles a combination of an optical particle counter (OPC), which measures submicrometer- to micrometer-sized particles, and a scanning mobility particle sizer (SMPS), which measures nanometer- to submicrometer-sized particle, has been suggested⁵.

Moreover, nanomaterial agglomerates generate complex shapes. However, most instruments are calibrated using monodispersed spherical polystyrene latex particles, making it necessary to evaluate the instrument performance using complex-shaped particles such as nanomaterial particles.

The purpose of this study was to evaluate the performance of two newly developed portable instruments (an OPC and an SMPS) for nanomaterial aerosol measurements by comparison with conventional instruments.

Methods

Aerosol measuring instruments

An optical particle sizer (OPS, Model 3330, TSI Inc.) and a portable SMPS (NanoScan, Model 3910, TSI Inc.)^{6,7} were recently developed and marketed as new types of OPC and SMPS, respectively. Table 1 shows the specifications of the newly-developed OPS and NanoScan, together with the widely-used conventional OPC (KR-12A, Rion Co.) and SMPS (Model 3936L10, TSI Inc.) for comparison. To distinguish between the new and old SMPS instruments, the newly developed SMPS will be referred to as NanoScan.

The newly developed instruments have several advantages. The OPS measures particle concentrations in 16 size channels, while the OPC has only six size channels. Moreover, the OPS operates well in dusty environments

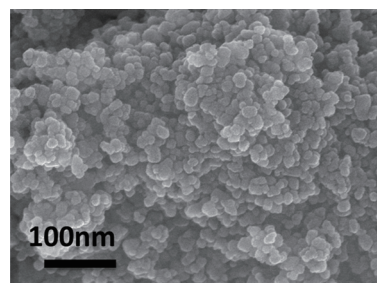


Fig. 1. SEM image of nano-TiO₂ P25 powder.

(up to 7,000 particles cm⁻³). The NanoScan is portable and battery-operated. These advantages potentially facilitate the measurement of the size distribution of nanometer to submicrometer particles and a combination of the OPS and the NanoScan has already been used for environmental measurements in workplaces handling nanomaterials⁸.

When using an SMPS, a coarse particle removal inlet (e.g., impactor or cyclone) is commonly attached to protect the instrument from high concentrations of coarse particles and to prevent measurement errors⁹. The NanoScan has a cyclone inlet composed of a cyclone with a cut-off diameter of 0.5 μ m and an orifice. The aerosol particles first pass through the orifice in which the aerosol sampling flow rate is controlled, and then the coarse particles are removed in the cyclone. The cyclone inlet cannot be detached from the main body because the NanoScan is operated under a fixed pressure drop across the inlet cyclone. On the other hand, a variety of inlet option can be attached to the SMPS. In this study, a cyclone with about 3 μ m cut-off point diameter operated at a flow rate of 2.45 L min⁻¹ (URG-2000-30ED, URG Co.) was used in the SMPS.

All instruments used in this study were calibrated within the periods recommended by the manufacturer and maintained before and after the measurements according to the service manual.

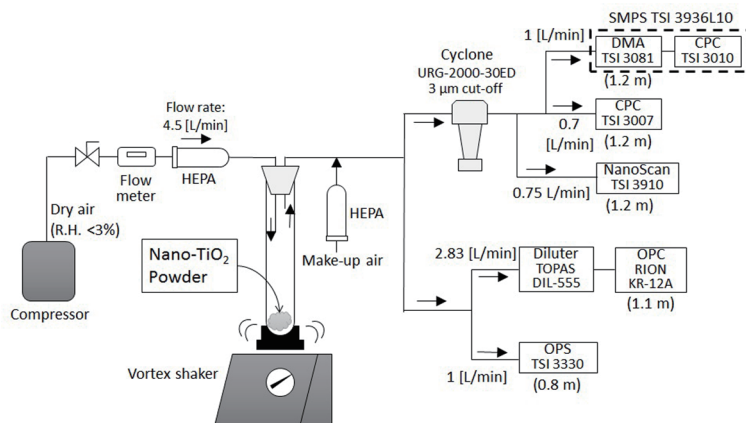


Fig. 2. Schematic diagram of the nano-TiO₂ aerosol generating and measuring system. The values in parentheses indicate the total lengths of the tubing.

The data obtained by the OPS and NanoScan were compared with the obtained by the OPC and the SMPS, respectively.

Test aerosol particles and tubing

Figure 1 shows nano-TiO₂ powder (AEROXIDE[®] P25, Evonik Industries) photographed by a field-emission scanning electron microscope (FE-SEM; S-4700, Hitachi Co.). The diameters of the primary particles were observed one by one (210 particles in total) with image processing software (Winroof, Mitani Co.) and their median diameter was about 26 nm.

Figure 2 shows the experimental system to measure the nano-TiO₂ aerosol particles. Polydispersed nano-TiO₂ aerosol particles were used for evaluating the performance of the aerosol sizers. The aerosols were generated from the nano-TiO₂ P25 powder using a vortex shaker^{8–12} and aerosolized as follows. One cm³ of the powder was placed in a glass test tube and agitated using a vortex shaker at a constant rotational speed (2,750 rpm), after which the suspended particles were delivered to the aerosol sizers by HEPA-filtered air. Conductive silicone tubing was used to avoid the deposition of charged particles by electrostatic forces in the sampling line during transport. The total lengths of the tubing between the outlet of the test tube and the inlet of each instrument were about 0.8 m for the OPS, 1.1 m for the OPC, and 1.2 m for the SMPS and the NanoScan. The concentrations and size distributions of the nano-TiO₂ aerosol particles were maintained during the performance evaluation¹².

All instruments (OPC, OPS, SMPS, and NanoScan) were placed in parallel, and the measured data were compared. The size distributions were continuously measured

for 30 min from 1 to 31 min after commencement of agitation, same as for the vortex shaker dustiness test⁴). The SMPS measured the size distribution at 3 min intervals, while the other sizers measured it at 1 min intervals. In this study, the aerosol and sheath flow rates of the SMPS were set to 1.0 and 3.0 L min⁻¹, respectively. The SMPS scan and retrace times were 160 and 15 s, respectively. For the data post-processing by the Aerosol Instrument Manager software (TSI Inc.), we did not use the multiple charge, diffusion loss, and aggregate correction functions. These settings were the same as for other measurements of nanomaterial aerosol particles with vortex shaker methods^{4, 11–13}). A similar size distribution was obtained even though the measurements were carried out in different research institutes using different models of the SMPS^{12, 13}).

Indoor aerosols in a laboratory with windows at the Naborito District of National Institute of Occupational Safety and Health, Japan (JNIOH), located in an urban residential area, were also measured for intercomparison. In this case, the aerosols were partly influenced by the outdoor environment, since the windows were not sealed well and there were people coming in and out of the room during the experiment. The representative particle concentrations of the indoor aerosols were between 6,000 to 14,000 particles cm⁻³, checked by a CPC (Model 3007, TSI Inc.). For the measurements using the SMPS and the NanoScan the air was sampled at the same point and transported to the instruments through conductive silicon tubing and the URG cyclone. For the OPC and OPS, the air was drawn without tubing, but the position of the sampling inlets was adjusted to be almost the same.

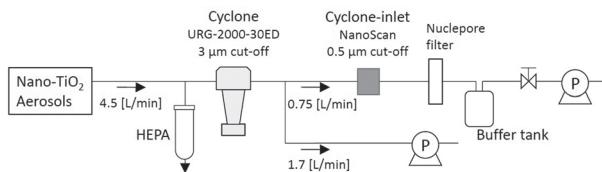


Fig. 3. Schematic diagram of the nano-TiO₂ P25 aerosol sampling system for FE-SEM observation.

Scanning electron microscope (SEM) observation

Aerosol particles passing through the URG cyclone and the NanoScan cyclone inlet, which represented the particles introduced in the NanoScan (referred to as NanoScan sample), were collected on Nuclepore membrane filters with 80 nm pore size for FE-SEM observations (Fig. 3). Aerosol particles passing only through the URG cyclone, which represented the aerosol particles introduced in the SMPS (referred to as SMPS sample), were also collected. The samples were collected for 20 min starting 1 min after the start of the nano-TiO₂ aerosol generation at a flow rate of 0.75 L min⁻¹ (the same as the NanoScan inlet flow).

After collecting the nano-TiO₂ aerosol particles, a portion of the filters was fixed onto an aluminum stage with carbon tape and coated with Pt-Pb by an ion sputter (E-1030, Hitachi Co.). The samples were observed with the FE-SEM under a 10 kV accelerating voltage and a 12 mm working distance.

Results and Discussion

OPS vs. OPC

The results showed that the particle concentration and size distribution of the nano-TiO₂ aerosol particles measured by the OPS were very similar to the OPC (Fig. 4). The OPS data showed three small peaks at 1, 2, and 6 μm in optical diameter, while the OPC showed only one peak around 3 μm. However, such differences might be within the error.

OPCs (including the OPS) have advantages, such as particle-size-distribution measurements with a high time resolution, for a wide size range, and at a relatively low cost. However, the optical diameter does not necessarily correspond to the geometric diameter, which may be related to the toxic effects, or to the aerodynamic diameter, which is generally related with the respirable fractions, filtration efficiency, and aerosol fate. Therefore, in future work, the accumulation of information on the relationships between the optical and the geometric diameter (through microscopic observation) and the optical and the aerody-

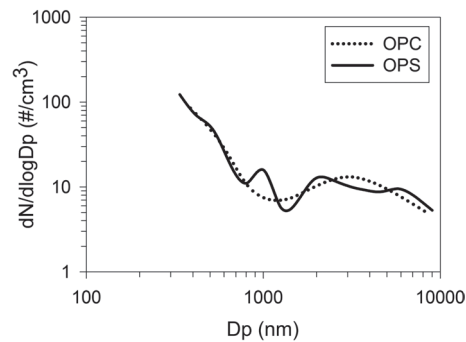


Fig. 4. Number-size distributions of nano-TiO₂ P25 aerosol particles measured with OPS and OPC.

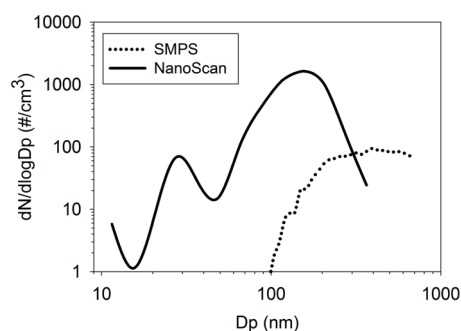


Fig. 5. Number-size distributions of nano-TiO₂ P25 aerosols measured with NanoScan and SMPS.

namic diameter (using an aerodynamic particle sizer) will be helpful.

NanoScan vs. SMPS

There were obvious differences in the size distributions of nano-TiO₂ according to the NanoScan and the SMPS (Fig. 5). The SMPS showed a size distribution with a mode around 300 nm, with most particles detected in the size range above 100 nm. Oppositely, the NanoScan showed a bimodal size distribution with two modes around 30 and 100 nm. The total particle concentrations in the size range of 10–400 nm measured with the NanoScan were at least one order of magnitude greater than the measured with the SMPS. Even when the data post-processing of the SMPS such as multiple charge, diffusion, and agglomeration corrections were applied, the obvious differences in the size distributions could not be explained.

Figure 6 shows the SEM images of nano-TiO₂ P25 aerosol particles from the NanoScan and the SMPS samples. The NanoScan sample showed smaller particles with less than 100 nm in diameter (Fig. 6 (a)), while no such small particles were found in the SMPS sample (Fig. 6 (b)). Ad-

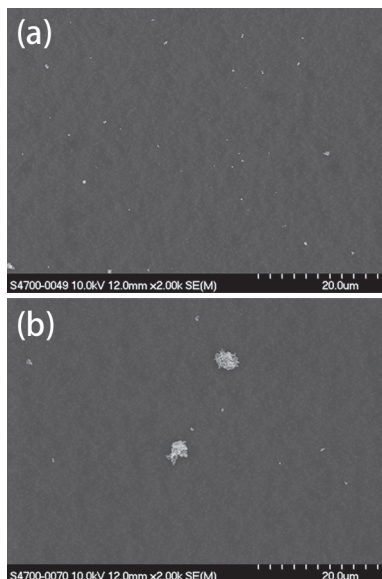


Fig. 6. Nano-TiO₂ P25 aerosols passing through the URG cyclone and the NanoScan cyclone inlet (a), and only passing through the URG cyclone (b). The images were observed at a 2,000-fold magnification with FE-SEM.

ditionally, there were more particles on the NanoScan filter than on the SMPS filter. Although the first peak appeared clearly around 30 nm (Fig. 4), such small particles, whose size is similar to the primary particles, were not found by the FE-SEM.

A possible reason for the differences between the SMPS and NanoScan results (Fig. 5) is that the cyclone inlet of the NanoScan acted as a disperser of the nanomaterial agglomerates. The dispersion of agglomerated particles in the air occurs by rapid changes in the air stream such as rapid acceleration, high shear fields, extensional flows, and collision between particles or between particles and a wall surface. As an example, an orifice is known as a disperser of agglomerated particles¹⁴, due to the dispersion force associated with rapid contracting and expanding of air in front and behind the orifice.

The pressure drop across the NanoScan cyclone inlet was about 5.0 kPa at a flow rate of 0.75 L min⁻¹ under atmospheric conditions of about 20°C and 1,000 hPa, while across the URG cyclone it was about 0.15 kPa at a flow rate of 2.45 L min⁻¹, under the same atmospheric conditions. The pressure loss in the NanoScan cyclone inlet was about 30 times larger than for the URG cyclone, suggesting that the higher pressure loss would increase the dispersion of the agglomerates¹⁴, although the inner structure of the NanoScan cyclone is not originally open.

Thus, the cyclone inlet of the NanoScan exerted

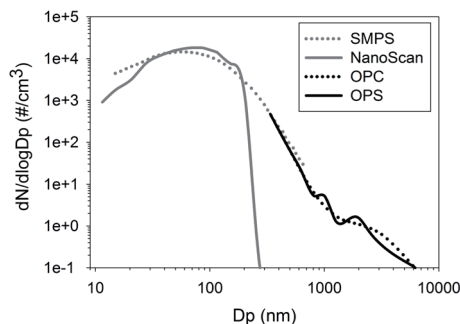


Fig. 7. Number-size distributions of indoor aerosol particles.

stronger external force to particles. Consequently, the concentration could increase through the breakup of weakly agglomerated particles, with the modes shifting to smaller sizes. Therefore, we should care about the possibility of dispersion in the cyclone inlet, and recommend testing for inlet effects on targeted nanomaterials.

Measurement of indoor aerosols

The measured size distributions for the indoor aerosols were consistent with each other (Fig. 7), except for particles larger than 200 nm measured by the NanoScan.

Aerosols in the ambient air are generally composed of single particles (e.g., sulfate) or strongly linked aggregate particles (e.g., soot)¹⁶. It is therefore suggested that such particles were not easily broken up by the cyclone inlet of the NanoScan and consequently their size distribution is similar for the NanoScan and SMPS measurements. However, our results (Fig. 7) show that the concentration of particles larger than 200 nm measured by the NanoScan was considerably lower than for the SMPS. Similar trends were observed in the manufacturer's reports^{7, 15} when the concentration of particles with a size close to the upper limit was substantially lower than the total concentration. Therefore, the size distribution of such particles measured by the NanoScan requires special care.

Conclusion

We compared the aerosol monitoring capability of novel (OPS and NanoScan) and conventional instruments (OPC and SMPS), using nano-TiO₂ powder as test aerosol particles. The data measured by the OPS were comparable to the OPC. In contrast, the data from the NanoScan were clearly different from those by the SMPS. A possible reason for these differences is that the cyclone inlet of the NanoScan acted as a disperser of nanomaterial agglomerates. Consequently, the concentration could increase

through the breakup of weakly agglomerated particles, with the modes shifting to smaller sizes. Thus, we must consider the possibility of dispersion by the cyclone inlet and recommended the testing for inlet effects on targeted nanomaterials. When indoor aerosol particles were measured, the NanoScan results were similar to the SMPS.

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